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Fire Extinguishing Composition and Process

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Field of Invention

- 5 This invention relates to compositions for use in preventing and extinguishing fires based on the combustion of combustible materials. More particularly, it relates to such compositions that are highly effective and "environmentally safe".
- 10 Specifically, the compositions of this invention have little or no effect on the ozone layer depletion process; and make no or very little contribution to the global warming process known as the "greenhouse effect". Although these compositions have minimal
- 15 effect in these areas, they are extremely effective in preventing and extinguishing fires, particularly fires in enclosed spaces.

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Background of the Invention and Prior Art

- 20 In preventing or extinguishing fires, two important elements must be considered for success: (1) separating the combustibles from air; and (2) avoiding or reducing the temperature necessary for combustion to proceed. Thus, one can smother small fires with
- 25 blankets or with foams to cover the burning surfaces to isolate the combustibles from the oxygen in the air. In the customary process of pouring water on the burning surfaces to put out the fire, the main element is reducing temperature to a point where combustion
- 30 cannot proceed. Obviously, some smothering or separation of combustibles from air also occurs in the water situation.

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- 35 The particular process used to extinguish fires depends upon several items, e.g. the location of the fire, the combustibles involved, the size of the

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fire, etc. In fixed enclosures such as computer rooms, storage vaults, rare book library rooms, petroleum pipeline pumping stations and the like, halogenated hydrocarbon fire extinguishing agents are currently preferred. These halogenated hydrocarbon fire extinguishing agents are not only effective for such fires, but also cause little, if any, damage to the room or its contents. This contrasts to the well-known "water damage" that can sometimes exceed the fire damage when the customary water pouring process is used.

The halogenated hydrocarbon fire extinguishing agents that are currently most popular are the bromine-containing halocarbons, e.g. bromotrifluoromethane (CF_3Br , Halon 1301) and bromochlorodifluoromethane (CF_2ClBr , Halon 1211). It is believed that these bromine-containing fire extinguishing agents are highly effective in extinguishing fires in progress because, at the elevated temperatures involved in the combustion, these compounds decompose to form products containing bromine atoms which effectively interfere with the self-sustaining free radical combustion process and, thereby, extinguish the fire. These bromine-containing halocarbons may be dispensed from portable equipment or from an automatic room flooding system activated by a fire detector.

In many situations, enclosed spaces are involved. Thus, fires may occur in rooms, vaults, enclosed machines, ovens, containers, storage tanks, bins and like areas.

The use of an effective amount of fire extinguishing agent in an enclosed space involves two situations. In one situation, the fire extinguishing agent is introduced into the enclosed space to

extinguish an existing fire; the second situation is to provide an ever-present atmosphere containing the fire "extinguishing" or, more accurately prevention agent in such an amount that fire cannot be initiated nor sustained. Thus, in U.S. Patent 3,844,354, Larsen suggests the use of chloropentafluoroethane ($\text{CF}_3\text{-CF}_2\text{Cl}$) in a total flooding system (TFS) to extinguish fires in a fixed enclosure, the chloropentafluoroethane being introduced into the fixed enclosure to maintain its concentration at less than 15%. On the other hand, in U.S. Patent 3,715,438, Huggett discloses creating an atmosphere in a fixed enclosure which does not sustain combustion. Huggett provides an atmosphere consisting essentially of air, a perfluorocarbon selected from carbon tetrafluoride, hexafluoroethane, octafluoropropane and mixtures thereof.

It has also been known that bromine-containing halocarbons such as Halon 1211 can be used to provide an atmosphere that will not support combustion. However, the high cost due to bromine content and the toxicity to humans i.e. cardiac sensitization at relatively low levels (e.g. Halon 1211 cannot be used above 1-2 %) make the bromine-containing materials unattractive for long term use.

In recent years, even more serious objections to the use of brominated halocarbon fire extinguishants has arisen. The depletion of the stratospheric ozone layer, and particularly the role of chlorofluorocarbons (CFC's) have led to great interest in developing alternative refrigerants, solvents, blowing agents, etc. It is now believed that bromine-containing halocarbons such as Halon 1301 and Halon 1211 are at least as active as chlorofluorocarbons in the ozone layer depletion process.

While perfluorocarbons such as those suggested by Huggett, cited above, are believed not to have as much effect upon the ozone depletion process as chlorofluorocarbons, their extraordinarily high stability makes them suspect in another environmental area, that of "greenhouse effect". This effect is caused by accumulation of gases that provide a shield against heat transfer and results in the undesirable warming of the earth's surface.

There is, therefore, a need for an effective fire extinguishing composition and process which contributes little or nothing to the stratospheric ozone depletion process or to the "greenhouse effect".

It is an object of the present invention to provide such a fire extinguishing composition; and to provide a process for preventing and controlling fire in a fixed enclosure by introducing into said fixed enclosure, an effective amount of the composition.

Summary of Invention

The present invention is based on the finding that an effective amount of a composition comprising at least one partially fluoro-substituted ethane selected from the group of pentafluoroethane ($\text{CF}_3\text{-CHF}_2$), also known as HFC-125, the tetrafluoroethanes ($\text{CHF}_2\text{-CHF}_2$ and $\text{CF}_3\text{-CH}_2\text{F}$), also known as HFC-134 and HFC-134a, the chlorotetrafluoroethanes ($\text{CF}_3\text{-CFHCl}$ and $\text{CF}_2\text{Cl-CF}_2\text{H}$), also known as HCFC-124 and HCFC-124a, the dichlorotrifluoroethanes ($\text{CF}_3\text{-CHCl}_2$ and $\text{CF}_2\text{Cl-CHFCl}$), also known as HCFC-123 and HCFC-123a, and the dichlorodifluoroethanes (CHFCl-CHFCl and $\text{CCl}_2\text{F-CH}_2\text{F}$), also known as HCFC-132 and HCFC-132c will prevent and/or extinguish fire based on the combustion of combustible materials, particularly in an enclosed

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space, without adversely affecting the atmosphere from the standpoint of ozone depletion or "greenhouse effect". The preferred group comprises $\text{CF}_3\text{-CHF}_2$, $\text{CF}_3\text{-CH}_2\text{F}$ and $\text{CF}_3\text{-CHCl}_2$.

- 5 The partially fluoro-substituted ethanes above may be used in conjunction with as little as 1% of at least one halogenated hydrocarbon selected from the group of difluoromethane (HFC-32), chlorodifluoromethane (HCFC-22),
- 10 2,2-dichloro-1,1,1-trifluoroethane (HCFC-123),
1,2-dichloro-1,1,2-trifluoroethane (HCFC-123a),
2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124),
1-chloro-1,1,2,2-tetrafluoroethane (HCFC-124a),
pentafluoroethane (HFC-125), 1,1,2,2-tetrafluoroethane
- 15 (HFC-134), 1,1,1,2-tetrafluoroethane (HFC-134a),
3,3-dichloro-1,1,1,2,2-pentafluoropropane (HCFC-225ca),
1,3-dichloro-1,1,2,2,3-pentafluoropropane (HCFC-225cb),
2,2-dichloro-1,1,1,3,3-pentafluoropropane (HCFC-225aa),
2,3-dichloro-1,1,1,3,3-pentafluoropropane (HCFC-225da),
- 20 1,1,1,2,2,3,3-heptafluoropropane (HFC-227ca),
1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea),
1,1,1,2,3,3,3-hexafluoropropane (HFC-236ea),
1,1,1,3,3,3,3-hexafluoropropane (HFC-236fa),
1,1,1,2,2,3,3-hexafluoropropane (HFC-236cb),
- 25 1,1,2,2,3,3,3-hexafluoropropane (HFC-236ca),
1,2-dichloro-1,2-difluoroethane (HCFC-132),
1,1-dichloro-1,2-difluoroethane (HCFC-132c),
3-chloro-1,1,2,2,3-pentafluoropropane (HCFC-235ca),
3-chloro-1,1,1,2,2-pentafluoropropane (HCFC-235cb),
- 30 1-chloro-1,1,2,2,3-pentafluoropropane (HCFC-235cc),
3-chloro-1,1,1,3,3-pentafluoropropane (HCFC-235fa),
3-chloro-1,1,1,2,2,3-hexafluoropropane (HCFC-226ca),
1-chloro-1,1,2,2,3,3-hexafluoropropane (HCFC-226cb),
2-chloro-1,1,1,3,3,3-hexafluoropropane (HCFC-226da),

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3-chloro-1,1,1,2,3,3-hexafluoropropane (HCFC-226ea),
and 2-chloro-1,1,1,2,3,3-hexafluoropropane
(HCFC-226ba).

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5 Preferred Embodiments

The partially fluoro-substituted ethanes, when added in adequate amounts to the air in a confined space, eliminates the combustion-sustaining properties of the air and suppresses the combustion of flammable
10 materials, such as paper, cloth, wood, flammable liquids, and plastic items, which may be present in the enclosed compartment.

These fluoroethanes are extremely stable and chemically inert. They do not decompose at
15 temperatures as high as 350°C to produce corrosive or toxic products and cannot be ignited even in pure oxygen so that they continue to be effective as a flame suppressant at the ignition temperatures of the combustible items present in the compartment.

20 The particularly preferred fluoroethanes HFC-125, HFC-134, and HFC-134a, as well as HCFC-124 are additionally advantageous because of their low boiling points, i.e. boiling points at normal atmospheric
31 pressure of less than -12°C. Thus, at any low
25 environmental temperature likely to be encountered, these gases will not liquefy and will not, thereby, diminish the fire preventive properties of the modified air. In fact, any material having such a low boiling point would be suitable as a refrigerant.

30 The fluoroethane HFC-125 is also characterized by an extremely low boiling point and high vapor pressure, i.e. above 164 psig at 21°C. This permits HFC-125 to act as its own propellant in
40 "hand-held" fire extinguishers. Pentafluoroethane
35 (HFC-125) may also be used with other materials such as

those disclosed on pages 5 and 6 of this specification to act as the propellant and co-extinguishant for these materials of lower vapor pressure. Alternatively, these other materials of lower vapor pressure may be
5 propelled from a portable fire extinguisher by the usual propellants, i.e. nitrogen or carbon dioxide. Their relatively low toxicity and their short atmospheric lifetime (with little effect on the global warming potential) compared to the perfluoroalkanes
10 (with lifetimes of over 500 years) make these fluoroethanes ideal for this fire-extinguisher use.

To eliminate the combustion-sustaining properties of the air in the confined space situation, the gas or gases should be added in an amount which
15 will impart to the modified air a heat capacity per mole of total oxygen present sufficient to suppress or prevent combustion of the flammable, non-self-sustaining materials present in the enclosed environment.

20 The minimum heat capacity required to suppress combustion varies with the combustibility of the particular flammable materials present in the confined space. It is well known that the combustibility of materials, namely their capability
25 for igniting and maintaining sustained combustion under a given set of environmental conditions, varies according to chemical composition and certain physical properties, such as surface area relative to volume, heat capacity, porosity, and the like. Thus, thin,
30 porous paper such as tissue paper is considerably more combustible than a block of wood.

In general, a heat capacity of about 40 cal./°C and constant pressure per mole of oxygen is more than adequate to prevent or suppress the
35 combustion of materials of relatively moderate

combustibility, such as wood and plastics. More
combustible materials, such as paper, cloth, and some
volatile flammable liquids, generally require that the
fluoroethane be added in an amount sufficient to impart
5 a higher heat capacity. It is also desirable to
provide an extra margin of safety by imparting a heat
capacity in excess of minimum requirements for the
particular flammable materials. A minimum heat
capacity of 45 cal./°C per mole of oxygen is generally
10 adequate for moderately combustible materials and a
minimum of about 50 cal./°C per mole of oxygen for
highly flammable materials. More can be added if
desired but, in general, an amount imparting a heat
capacity higher than about 55 cal./°C per mole of total
15 oxygen adds substantially to the cost without any
substantial further increase in the fire safety factor.

Heat capacity per mole of total oxygen can be
determined by the formula:

$$C_p^* = (C_p)_{O_2} + \sum \frac{P_z}{P_{O_2}} (C_p)_z$$

wherein:

C_p^* = total heat capacity per mole of oxygen at
constant pressure;

P_{O_2} = partial pressure of oxygen;

P_z = partial pressure of other gas;

$(C_p)_z$ = heat capacity of other gas at constant
pressure.

The boiling points of the fluoroethanes used
in this invention and the mole percents required to
impart to air heat capacities (C_p) of 40 and 50 cal./°C
at a temperature of 25°C and constant pressure while

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maintaining a 20% and 16 % oxygen content are tabulated below:

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	FC	Boiling point, °C.	20 % O ₂		16 % O ₂
			C _p =40 vol	C _p =50 vol	C _p =50 vol
			percent	percent	percent
5	125	-48.5	6.5	19.5	6.5
	134	-19.7	8.5	25.0	8.5
10	134a	-26.5	7.0	20.5	7.0
	124	-12.0	6.5	19.0	6.5
	124a	-10.2	6.5	19.0	6.5
	123	27.9	6.0	17.0	6.0
	123a	30.0	6.0	17.5	6.0
15	132	59.0	7.0	20.5	7.0
	132c	48.4	6.5	19.0	6.5

P Introduction of the appropriate gaseous fluoroethanes is easily accomplished by metering appropriate quantities of the gas or gases into the enclosed air-containing compartment.

The air in the compartment can be treated at any time that it appears desirable. The modified air can be used continuously if a threat of fire is constantly present or if the particular environment is such that the fire hazard must be kept at an absolute minimum; or the modified air can be used as an emergency measure if a threat of fire develops.

The invention will be more clearly understood by referring to the examples which follow. The unexpected effects of the fluoroethane compositions, in suppressing and combatting fire, as well as its compatability with the ozone layer and its relatively low "greenhouse effect", when compared to other fire-combatting gases, particularly the perfluoroalkanes and Halon 1211, are shown in the examples.

Example 1 - Fire Extinguishing Concentrations

The fire extinguishing concentration of the fluoroethane compositions compared to several controls, was determined by the ICI Cup Burner method. This method is described in "Measurement of Flame-Extinguishing Concentrations" R. Hirst and K. Booth, Fire Technology, vol. 13(4): 296-315 (1977).

Specifically, an air stream is passed at 40 liters/minute through an outer chimney (8.5 cm. I. D. by 53 cm. tall) from a glass bead distributor at its base. A fuel cup burner (3.1 cm. O.D. and 2.15 cm. I.D.) is positioned within the chimney at 30.5 cm. below the top edge of the chimney. The fire extinguishing agent is added to the air stream prior to its entry into the glass bead distributor while the air flow rate is maintained at 40 liters/minute for all tests. The air and agent flow rates are measured using calibrated rotameters.

Each test is conducted by adjusting the fuel level in the reservoir to bring the liquid fuel level in the cup burner just even with the ground glass lip on the burner cup. With the air flow rate maintained at 40 liters/minute, the fuel in the cup burner is ignited. The fire extinguishing agent is added in measured increments until the flame is extinguished. The fire extinguishing concentration is determined from the following equation:

$$\text{Extinguishing concentration} = \frac{F_1}{F_1 + F_2} \times 100$$

where F_1 = Agent flow rate
 F_2 = Air flow rate

P Two different fuels are used, heptane and methanol; and the average of several values of agent flow rate at extinguishment is used for the following table.

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Table 1

Extinguishing Concentrations of Certain Fluoroethane Compositions Compared to Other Agents

10	<u>Agent</u>	<u>Fuel</u>		<u>Flow Rate</u>		
		Heptane Methanol				
		Extinguishing	Conc.	Air	Agent	
		(vol. %)	(vol. %)	(l/min)	(l/min)	
	<u>Fe#</u>				<u>Hept.</u>	<u>Meth.</u>
15	HCFC-123	7.1	10.6	40.1	3.06	4.75
	HCFC-123a	7.7	10.1	40.1	3.37	5.11
	HCFC-124	8.0	11.9	40.1	3.49	5.45
	HFC-125	10.1	13.0	40.1	4.51	5.99
	HFC-134a	11.5	15.7	40.1	5.22	7.48
20						
	CF ₄	20.5	23.5	40.1	10.31	12.34
	C ₂ F ₆	8.7	11.5	40.1	3.81	5.22
	H-1301*	4.2	8.6	40.1	1.77	3.77
	H-1211**	6.2	8.5	40.1	2.64	3.72
25	CHF ₂ Cl	13.6	22.5	40.1	6.31	11.64

* CF₃Br

** CF₂ClBr

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Example 2 Cardiac Sensitivity

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The cardiac sensitivity or toxicity of the
fluoroethanes, compared to several controls, was
5 determined using the methods described in "Relative
Effects of Haloforms and Epinephrine on Cardiac
Automaticity" R. M. Hopkins and J. C. Krantz, Jr.,
Anesthesia and Analgesia, vol. 47 no. 1 (1968) and
1, 2 "Cardiac Arrhythmias and Aerosol 'Sniffing'" C. F.
10 Reinhardt et al. Arch. Environ. Health vol. 22
(February 1971).

Specifically, the cardiac sensitivity is
measured using unanesthetized, healthy dogs using the
general protocol set forth in the Reinhardt et al
15 article. First, for a limited period, the dog is
subjected to air flow through a semiclosed inhalation
system connected to a cylindrical face mask on the dog.
Then, epinephrine hydrochloride (adrenaline), diluted
with saline solution, is administered intravenously and
20 the electrocardiograph is recorded. Then air
containing various concentrations of the agent being
tested is administered followed by a second injection
of epinephrine. The concentrations of agent necessary
to produce a disturbance in the normal conduction of an
25 electrical impulse through the heart as characterized
by a serious cardiac arrhythmia, are shown in the
following table.

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Table 2

	<u>Agent</u>	<u>Threshold</u> <u>Cardiac Sensitivity</u> (vol. % in air)
5	HFC-134a	7.5
	H-1301*	7.5
	CHF ₂ Cl	5.0
	HCFC-124	2.5
	HCFC-123	1.9
10	H-1211**	1 to 2
	* CF ₃ Br	
	** CF ₂ ClBr	
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Example 3

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The ozone depletion potential (ODP) of the
fluoroethanes and various blends thereof, compared to
5 various controls, was calculated using the method
described in "The Relative Efficiency of a Number of
Halocarbon for Destroying Stratospheric Ozone" D. J.
Wuebles, Lawrence Livermore Laboratory report
UCID-18924, (January 1981) and "Chlorocarbon Emission
10 Scenarios: Potential Impact on Stratospheric Ozone" D.
J. Wuebles, Journal Geophysics Research, 88, 1433-1443
(1983).

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Basically, the ODP is the ratio of the
calculated ozone depletion in the stratosphere
15 resulting from the emission of a particular agent
compared to the ODP resulting from the same rate of
emission of FC-11 (CFC13) which is set at 1.0. Ozone
depletion is believed to be due to the migration of
compounds containing chlorine or bromine through the
20 troposphere into the stratosphere where these compounds
are photolyzed by UV radiation into chlorine or bromine
atoms. These atoms will destroy the ozone (O3)
molecules in a cyclical reaction where molecular oxygen
(O2) and [ClO] or [BrO] radicals are formed, those
25 radicals reacting with oxygen atoms formed by UV
radiation of O2 to reform chlorine or bromine atoms and
oxygen molecules, and the reformed chlorine or bromine
atoms then destroying additional ozone, etc., until
the radicals are finally scavenged from the
30 stratosphere. It is estimated that one chlorine atom
will destroy 10,000 ozone molecules and one bromine
atom will destroy 100,000 ozone molecules.

The ozone depletion potential is also
discussed in "Ultraviolet Absorption Cross-Sections of
35 Several Brominated Methanes and Ethanes" L. T. Molina,
M. J. Molina and F. S. Rowland" J. Phys. Chem. 86,

14 F 2672-2676 (1982); in Bivens et al. U.S. Patent
4,810,403; and in "Scientific Assessment of
F Stratospheric Ozone: 1989" U.N. Environment Programme
(21 August 1989).

5 In the following table, the ozone depletion
potentials are presented for the fluoroethanes used in
this invention and various controls.

Table 3

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	<u>Agent</u>	<u>Ozone Depletion Potential</u>
	HCFC-123	0.013
	HCFC-124	0.013
	HFC-125	0
15	HFC-134a	0
	HFC-134	0
	CF ₄	0
	C ₂ F ₆	0
	H-1301	10
20	CHF ₂ Cl	0.05
	H-1211	3
	CFC1 ₃	1
	CF ₃ -CF ₂ Cl	0.4

Example 4

The global warming potentials (GWP) of the fluoroethane and various blends thereof, compared to several controls, was determined using the method described in "Scientific Assessment of Stratospheric Ozone: 1989" sponsored by the U.N. Environment Programme.

The GWP, also known as the "greenhouse effect" is a phenomenon that occurs in the troposphere. It is calculated using a model that incorporates parameters based on the agent's atmospheric lifetime and its infra-red cross-section or its infra-red absorption strength per mole as measured with an infra-red spectrophotometer.

The general definition is:

$$\text{GWP} = \frac{\text{Calculated IR forcing due to agent}}{\text{Emission rate (steady state) of agent}}$$

divided by the same ratio of parameters for CFCl_3 .

In the following table, the GWP's are presented for the fluoroethanes and the controls.

Table 4

<u>Agent</u>	<u>Global Warming Potential</u>
HFC-134a	0.220
HFC-125	0.420
HCFC-124	0.080
HCFC-123	0.015
CF_4	greater than 5
C_2F_6	greater than 8
CHF_2Cl	0.29
CFCl_3	1.0
$\text{CF}_3\text{CF}_2\text{Cl}$	8.2